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Nano $CaCO_3$ Incorporated PVC-PMMA Blends for Mechanical Property Modification

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ABSTRACT

Polyvinyl chloride (PVC) is a thermoplastic polymer which has found widespread usage in rigid and flexible applications. However, the problems of poor impact strength, difficult processability and low thermal resistance restricts its utility and invites research studies to overcome the limitations. Several polymeric or non-polymeric modifiers, often referred to as impact modifiers or processing aids are used to overcome these confinements. However, when a non polymeric modifier is used, one of the properties of the polymer is enhanced but it induces deterioration in the other. Several polymeric modifiers for PVC property modification have already been reported in literature. In the present study, polymethyl methacrylate (PMMA) blended with PVC to modify its mechanical properties have been stated. An attempt has been made to enhance the mechanical parameters of the PVC-PMMA blend even further by the incorporation of nano calcium carbonate (nano CaCO3) in definite proportion with respect to a defined ratio mix of PVC:PMMA. It has been observed that the modulus and ultimate tensile strength increased significantly but the rise was not at the compensation of reduction in elongation at break and toughness. So, the dynamics of the property variation has been estimated over the range of added nanofiller nano CaCO3.

KEYWORDS:Polyvinyl chloride, Polymethyl methacrylate, Mechanical properties, Nano calcium carbonate

1. INTRODUCTION

Polyvinyl chloride (PVC) is one of the most commonly used materials in the world. It is used in versatile fields owing to its light weight, durability, flame resistance, abrasion resistance, excellent insulation behavior and many other properties which it offers [1]. It is also economical and finds extensive usage as a commodity plastic for various applications. However, the use of PVC becomes limited in cases where superior impact properties, processibility and high thermal resistance set in. To overcome these drawbacks of properties, the use of polymeric or non polymeric modifiers referred to as impact modifiers or processing aids are used widely as reported in several literature [2, 3]. But, by the usage of a non polymeric modifier, some of the properties of the polymer are deteriorated as a compensation for the improvement of others [4]. In case of PVC, several modifiers are used to overcome the drawbacks as mentioned [5]. Ganesh et al [6]reported the assessment of structural, thermal, dielectric and catalytic properties on silver nanoparticle incorporated PVC films. He analysed that the properties exhibited improved performance on incorporation of the nanoparticles. In a study [7], it was revealed that PVC composites containing well dispersed nanoclays produced lesser smoke and increased hardness. The introduction of copper or silver nanoparticles in PVC largely influences the antimicrobial property and photostability as shown by Braga et al [8]. The effect of nano $CaCO_3$ on the mechanical properties of PVC and PVC/Blendex was estimated by Cen et.al [9]. On addition of 0 – 15 phr nano $CaCO_3$ incorporation, the properties like impact strength, flexural modulus, Vicat softening point enhanced appreciably as observed. The preparation of metal – polymer nanocomposites by chemical reduction of metal ions was estimated by Dzhardimalieva et al [10]. In another study, the catalytic activity of polymer inorganic composite materials was analysed in a silver nanoparticle loaded matrix by Yan et. al. [11]. Additionally, the antifouling properties and desalination performance of magnetite nanoparticle incorporated PVC microfiltration membrane was extensively reported by Alghamdi et al [12].

The incorporation of methacrylates and acrylates in PVC exhibits a unique method to influence the mechanical and thermal properties of the same. Methacrylate and acrylate modified PVC behaves as equivalent to rubber toughening of glassy polymers [13]. When PVC is blended with polymethyl methacrylate (PMMA), the mechanical properties of the former are largely influenced by increased modulus and ultimate tensile strength [14]. With this basic observation, the present study intends to improve the properties of PVC even further in terms of modulus and ultimate tensile strength alongwith elongation at break and toughness by incorporating nano calcium carbonate within it and estimate the dynamics of the incorporated system over a range of added nanofiller.

The formation of nanocomposites in the arena of Polymer Science and Technology has been a prominent example of synergism in properties [15, 16]. It provides an effective approach towards enhanced performance and creation of new functionalities. The resulting polymer nanocomposites benefit from the advantages of both the polymer matrix and reinforcement phase [17]. With this perception, the nanofiller, nano $CaCO_3$, has been incorporated in poly(methyl methacrylate) (PMMA) blended PVC matrix to observe the variation in mechanical properties with increasing proportion of the nanofiller.

In the present study, an endeavour has been made to modify and enhace the mechanical properties of PVC – PMMA 80:20 blend in terms of its modulus, ultimate tensile strength, elongation at break and toughness by incorporating nano calcium carbonate ($CaCO_3$) as the nanofiller. The nanofiller added had a proportionate variation of 3 to 15 phr in the blended system. It is proposed that the augmented property parameters subsequently leads to the superior applications of PVC in versatile sectors.

2. EXPERIMENTAL

A. Materials

PVC resin (grade K 67) was procured from M/s Kalpana Industries Ltd. and was used as the major matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulphate (TBLS) procured from M/s Kalpana Industries Ltd. (Daman, India) were used as suitable plasticizers and stabilizers respectively. Methyl methacrylate from M/s Burgoyne (India) was used as polymeric modifier of PVC. Nano calcium carbonate which was used as the nanofiller was supplied from Reinste Nanoventures Pvt. Ltd. Benzoyl peroxide from Loba Chemie (India) was used as initiator for acrylic polymerization.

B. Methods

PVC resin (80 parts by weight) was taken in an air tight dry blender and mixed with 30 parts by volume of dioctyl phthalate (DOP) plasticizer and 2 parts by weight of tribasic lead sulphate (TBLS) heat stabilizer with respect to the amount of PVC resin taken. The methyl methacrylate monomer (20 parts by weight) premixed with benzoyl peroxide initiator (2 parts by weight) was added to the PVC mix along with the nano calcium carbonate filler and mixed thoroughly in the blender at a slightly elevated temperature unless a thoroughly mixed powder was obtained. Various batches were prepared varying the dose of the nanofiller from 3, 6, 9, 12 and 15 parts by weight. The prepared blends was then moulded by compression in a compression moulding machine into sheets under heat and pressure. It was then subjected for mechanical testing in Instron Universal tester.

Initially, the mould (0.95 m x 0.65 m x 0.001 m) with the mixed powdery content was heated at a temperature of 80ºC to initiate and propagate acrylate polymerisation. This was allowed to continue for 30 min. Subsequently, the temperature was raised to 160ºC while a pressure of 15 tons/cm^2 was maintained. The mould was then cooled down to 100ºC and kept for 30 min to ensure complete polymerization of butyl acrylate and nanomaterial dispersion. Consequently, the mould was allowed to cool down to the room temperature and the moulded sheet ejected [18].

C. Characterization

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties of modulus, ultimate tensile strength, elongation at break and toughness. In the process of measurement, ASTM D638 method was followed.

3. RESULTS AND DISCUSSIONS

The effect of nanomaterial influence (nano $CaCO_3$) on PVC-PMMA blended system in 80:20 ratio, has been analyzed in terms of modulus, ultimate tensile strength, elongation at break and toughness. The PVC – PMMA blended system in 80:20 ratio has been chosen due to its significant elongation at break and toughness values. On incorporation of the nanofiller moieties into the blended system, it is expected that there would be an augmentation of the rigidity parameters of modulus and ultimate tensile strength followed by a reduction in the flexibility parameters of percent elongation at break and toughness. In order to maintain the balance of all the mechanical parameters and to minimize the compensation loss of any of the properties, the 80:20 blended system of PVC-PMMA is opted within which the nano calcium carbonate (nano $CaCO_3$) is incorporated within the range of 3 to 15 phr. The mechanical parameters of 80:20 PVC-PMMA blended system as already reported in literature are depicted in Table 1.

Table 1: Mechanical parameters of 80:20 PVC-PMMA blended system

Properties	PVC:PMMA 100:0 (Base reference compound)	PVC:PMMA 80:20
Modulus (MPa)	35.18	397
Ultimate tensile strength (MPa)	7.8	12.3
Elongation at break (%)	130	320
Toughness (MPa)	6.9	5.9

A. Variation of modulus

In the initial PVC – PMMA blended system of 80:20 composition, the molecular interaction between the two participating polymers come into consideration. The properties exhibited by the PVC-PMMA blend system may be attributed to the two opposing forces operating simultaneously; the secondary valence force due to formation of hydrogen bonds through the chlorine in PVC which is strongly electronegative and the ester group hydrogen present in the methacrylate. The increase in modulus of the blend over unmodified PVC up to an optimum level of 20% PMMA incorporation may also be attributed to the intermolecular hydrogen bonding between the hydrogen of vinyl chloride chain unit with the ester carboxylate group [19]. This can be accounted for the possible miscibility of the two polymers and consequent rise in the rigidity parameters.

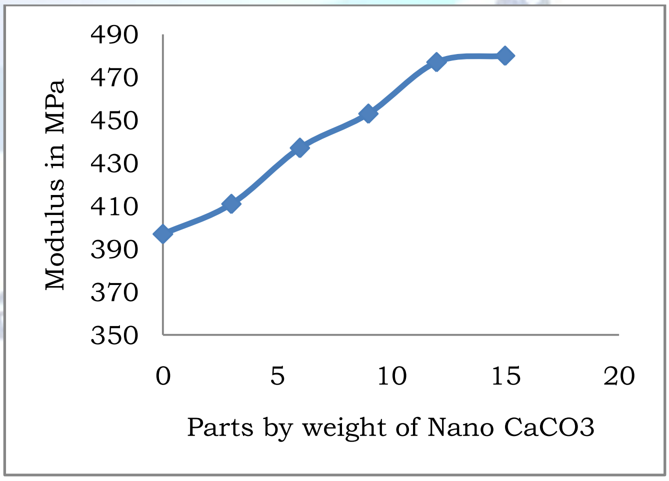

Figure 1: Variation of modulus with nano $CaCO_3$ dose

In Fig. 1, the variation of modulus of the nano calcium carbonate incorporated PVC – PMMA blend of 80:20 composition ratio with rise in the dose of nano $CaCO_3$ has been exhibited. Its rise is significant with the rise in dose of the nanofiller as observed. This is indicative of the fact that the nanoparticles with enhanced surface area get distributed within the PVC-PMMA blended matrix and augments the property resulting in augmented modulus. The rise in modulus from 397 MPa of the base blend to 480 MPa for 15 phr nanofiller incorporation is explicit and this signifies the modifying influence of nano $CaCO_3$ over a range of added nanofiller.

The overall value of modulus have been augmented by the addition of the nanofiller nano calcium carbonate over 3 to 15 phr range. It is accounted that the plasticization effect of the polymethyl methacrylate moieties tend to be non influential by the presence of the dispersed nanofiller which helps to raise the rigidity modulus parameter. The nano calcium carbonate exerts its reinforcing influence on the PVC-PMMA 80:20 blended system and aids in raising the modulus of the system well above the base reference compound. However, the modulus tends to level off at 15 phr which is indicative of reaching the optimization point of modulus in the entire system under consideration.

B.Variation of ultimate tensile strength

In Fig. 2, the rise in ultimate tensile strength (UTS) on increasing dose of nano calcium carbonate is represented and it is found to be in corroboration with the rise in modulus. The dynamical changes in the ultimate tensile strength have been studied from 3 to 15 parts by weight and a similar trend of rise is observed. There is a gradual rise from 12.3 MPa of unmodified PVC-PMMA blend to about 32.1 MPa at 15 parts of nano $CaCO_3$ incorporation. PVC-PMMA blend of 80:20 composition is substantially modified by the reinforcing properties of the nanomaterials which has been reflected by the significant rise in the mechanical characteristics.

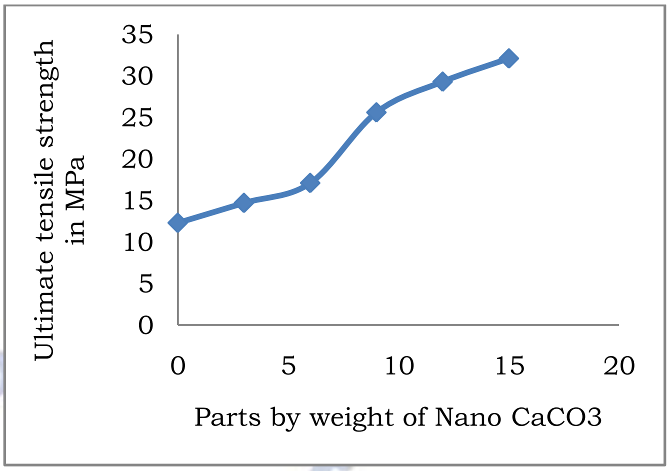

Figure 2: Variation of ultimate tensile strength with nano $CaCO_3$ dose

The strength properties show a gradual rise with increasing doses of nano calcium carbonate and tends to level off at 15 phr. As evidenced, the effect of nano $CaCO_3$ on PVC acts as the reinforcing filler to augment the strength of blended PVC and the saturation effect is reached at the higher doses. This parameter value increases more than two folds of the base compound. This emphasises the fact that nano calcium carbonate when used as nanofillers are very effective in modifying PVC and its blends owing to high molecular interaction and strong compatibility. So nano $CaCO_3$ contributes enormously to the modification of both the base polymer compound PVC as well as the PVC-PMMA 80:20 blend which is taken into consideration under this study.

C. Variation of elongation at break

The changes in elongation at break with the variation in nano calcium carbonate filler is depicted in Fig. 3. The percent elongation at break revealed a corroboration of value reduction by the combined influence of the rigid moieties of polymethyl metacrylate and nanofiller nano $CaCO_3$. The decrease from 159% to 113% in elongation at break may be attributed to the fact that within this range of concentration, there has been an increase in the packing density and proper free volume for chain slippage has not been generated.

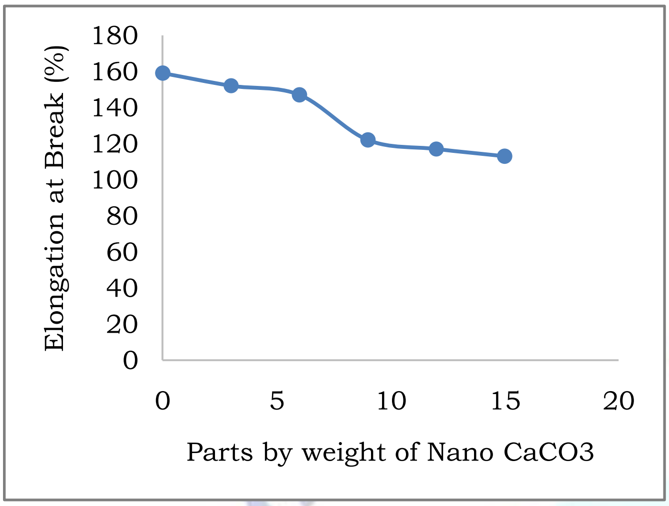

Figure 3: Variation of elongation at break with nano $CaCO_3$ dose

However, the reduction in the values of percentage elongation at break is indicative that the reduction is not quite significant as it would have been in the absence of the nanofiller. Hence, it explicit that the nano $CaCO_3$ acting as the nanofiller, raises the modulus and ultimate tensile strength with its increase but not at the compensation of the flexibility parameters. This establishes the fact that the nanofiller has a directing modifying influence on PVC as well as the 80:20 PVC-PMMA blend and contributes to the overall improvement of the mechanical properties of PVC. Thus, the combined influence of the polymethyl methacrylate polymer and nano calcium carbonate in varying doses on PVC is widely reflected within the range of nano $CaCO_3$ incorporation under study.

D.Variation of toughness

The flexibility parameter of toughness is depicted in Fig. 4. It is explicit that the values decrease very marginally from 5.9 to 5.1 and show an overall balance compared to the base reference PVC-PMMA compound of 80:20 composition. It is observed that there is no significant reduction due to the presence of the nanofiller although there is a decreasing trend in the toughness values due to the increasing concentration of the rigid nano $CaCO_3$ within the blended matrix. So, the nano calcium carbonate acting as the nanofiller, augments the strength parameters of PVC-PMMA 80:20 blend and consequently PVC with its increasing dose but not at the cost of elongation at break or toughness.

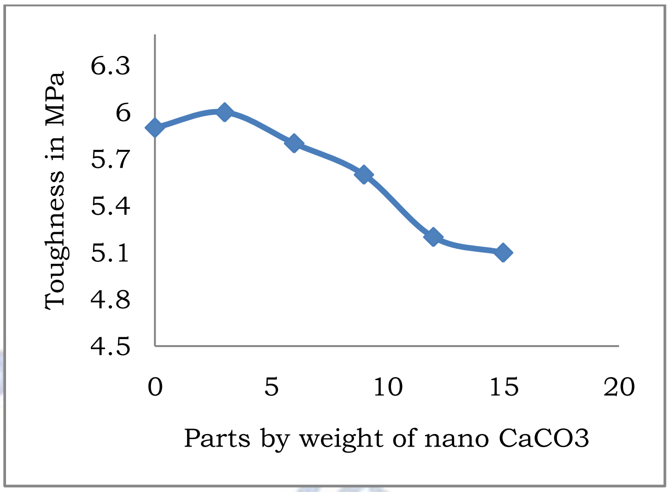

Figure 4: Variation of toughness with nano $CaCO_3$ dose

Evidently, the strength parameters of PVC and its 80:20 blend is raised with increasing dose of the nanofiller but it is not achieved at the cost of reduction of the flexibility parameters namely the elongation at break and toughness. This again establishes the fact that the polymeric modifier PMMA and the nanofiller nano calcium carbonate has a directing modifying influence on PVC and contributes to the overall enhancement of the mechanical properties of PVC. So the combined influence of the polymethyl methacrylate polymer and nano calcium carbonate on PVC is widely explicit within the range of the nanofiller incorporation under study.

4. CONCLUSION

In the present study, an endeavour has been made to analyze the changes in mechanical properties of PVC - poly (methyl methacrylate) blends in terms of its modulus, ultimate tensile strength, elongation at break and toughness by incorporating nano $CaCO_3$ as the nanofiller. The modification in the mechanical properties of PVC by way of blending with polymethyl methacrylate (PMMA) in 80:20 proportion incorporating nano $CaCO_3$ as the nanofiller in varying ranges, is estimated in the present study. The mechanical parameters of modulus, ultimate tensile strength, elongation at break and toughness exhibited a significant rise well above the values of the base reference compound under the directing influence of the nanofiller. Hence, mechanically modified PVC compound has been achieved wherein the strength properties of the polymer such as the modulus and ultimate tensile strength is modified not at the compensation of the flexibility parameters like elongation at break and toughness hence yielding mechanically improved PVC compounds in all aspects.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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